Electronic Supporting Information

Palladium-Catalyzed Polyannulation of Pyrazoles and Diynes toward Multifunctional Poly(indazole)s under Monomer Non-Stoichiometric Conditions

Qingqing Gao,†,‡,# Ting Han,†,‡,¶ Zijie Qiu,†,‡,# Ruoyao Zhang,†,‡ Jun Zhang,†,‡ Ryan T. K. Kwok,†,‡,§ Jacky W. Y Lam,†,‡,*,§ and Ben Zhong Tang†,‡,§,*,¶

†HKUST-Shenzhen Research Institute, No. 9 Yuexing 1st RD, South Area, Hi-tech Park, Nanshan, Shenzhen 518057, China;
‡ Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, Division of Life Science, Institute of Advanced Study and Department of Chemical and Biological Engineering;
§Center for Aggregation-Induced Emission, SCUT-HKUST Joint Research Institute, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China.
¶Center for AIE Research, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China

*Corresponding authors: Dr. J. W. Y. Lam and Prof. B. Z. Tang (E-mail: chjacky@ust.hk and tangbenz@ust.hk). Phone: +852-2358-7242 (7375). Fax: +852-2358-1594.
Table of Contents

Figure S1. High-resolution mass spectra of model compound 4.

Figure S2. High-resolution mass spectra of model compound 6.

Figure S3. $^1$H NMR spectrum of 6 in chloroform-$d$.

Figure S4. $^{13}$C NMR spectra of 6 chloroform-$d$.

Figure S5. IR spectra of (A) 2a, (B) model compound 4, (C) P1/2a.

Table S1. Crystal data and structure refinement for 4.

Figure S6. IR spectra of (A) 2b and (B) P1/2b.

Figure S7. $^1$H NMR spectra of (A) 2b, (B) 1 and (C) P1/2b in chloroform-$d$. The solvent peaks were marked with asterisks.

Figure S8. $^{13}$C NMR spectra of (A) 2b, (B) 1 and (C) P1/2b in chloroform-$d$. The solvent peaks were marked with asterisks.

Figure S9. IR spectra of (A) 2c and (B) P1/2c.

Figure S10. $^1$H NMR spectra of (A) 2c, (B) 1 and (C) P1/2c in chloroform-$d$. The solvent peaks were marked with asterisks.

Figure S11. $^{13}$C NMR spectra of (A) 2c, (B) 1 and (C) P1/2c in chloroform-$d$. The solvent peaks were marked with asterisks.

Figure S12. IR spectra of (A) 2d and (B) P1/2d.

Figure S13. $^1$H NMR spectra of (A) 2d in dichloromethane-$d_2$ and chloroform-$d$ and (B) 1 and (C) P1/2d in chloroform-$d$. The solvent peaks were marked with asterisks.

Figure S14. $^{13}$C NMR spectra of (A) 2d in dichloromethane-$d_2$ and chloroform-$d$ and (B) 1 and (C) P1/2d in chloroform-$d$. The solvent peaks were marked with asterisks.

Figure S15. Wavelength dependence of the refractive index of a thin film of P1/2a on the UV irradiation time.

Figure S16. (A) Absorption spectra and (B) emission spectra of P1/2 and 4 in THF solution. Solution concentration: 10 μM.

Figure S17. (A) Emission spectra of model compound 4 in THF/water mixtures with different water fractions ($f_w$). Solution concentration: 10 μM; excitation wavelength:
320 nm. (B) Plot of relative emission intensity ($I/I_0$) versus the water fraction of the THF/water mixtures of model compound 4.

**Figure S18.** (A) Emission spectra of P1/2a in THF/water mixtures with different water fractions ($f_w$). Solution concentration: 10 μM; excitation wavelength: 310 nm. (B) Plot of relative emission intensity ($I/I_0$) versus the water fraction of the THF/water mixtures of P1/2a. Inset: fluorescent photographs of P1/2a in THF solution and THF/water mixture with 90% water fraction taken under 365 nm UV illumination from a hand-held UV lamp.

**Figure S19.** Emission spectra of (A) P1/2b and (B) P1/2c in THF/water mixtures with water fractions ($f_w$) at 0% and 90%. Solution concentration: 10 μM; excitation wavelength: 310 nm.

**Figure S20.** (A) Emission spectra of P1/2d in THF/water mixtures with different water fractions ($f_w$). Solution concentration: 10 μM; excitation wavelength: 330 nm. (B) Plot of relative emission intensity ($I/I_0$) versus the water fraction of the THF/water mixtures of P1/2d. Inset: fluorescent photographs of P1/2d in THF solution and THF/water mixture with 90% water fraction taken under 365 nm UV illumination from a hand-held UV lamp.
**Figure S1.** High-resolution mass spectra of model compound 4.

**Figure S2.** High-resolution mass spectra of model compound 6.
Table S1. Crystal data and structure refinement for 4.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{32}$H$</em>{24}$N$_2$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>436.53</td>
</tr>
<tr>
<td>Temperature</td>
<td>296.09(13) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54184 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pna2$_1$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 12.7337(2)$ Å, $a = 90^\circ$. $b = 14.4626(2)$ Å, $b = 90^\circ$. $c = 13.1758(2)$ Å, $c = 90^\circ$.</td>
</tr>
<tr>
<td>Volume</td>
<td>2426.49(6) Å$^3$</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.195 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.534 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>920</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.540 to 71.160°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>$-15 \leq h \leq 10$, $-17 \leq k \leq 14$, $-16 \leq l \leq 15$</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>6902</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3966 [R(int) = 0.0139]</td>
</tr>
<tr>
<td>Completeness to theta = 67.684°</td>
<td>100.0 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.00000 and 0.75628</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3966 / 109 / 298</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.025</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0362, wR2 = 0.0947</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0390, wR2 = 0.0974</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.1(8)</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.0037(3)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.181 and -0.116 e.Å$^{-3}$</td>
</tr>
</tbody>
</table>
Figure S3. IR spectra of (A) 2a, (B) model compound 4, (C) P1/2a.

Figure S4. IR spectra of (A) 2b and (B) P1/2b.
Figure S5. $^1$H NMR spectra of (A) 2b and (B) 1 and (C) P1/2b in chloroform-$d$. The solvent peaks were marked with asterisks.

Figure S6. $^{13}$C NMR spectra of (A) 2b, (B) 1 and (C) P1/2b in chloroform-$d$. The solvent peaks were marked with asterisks.
Figure S7. IR spectra of (A) 2c and (B) P1/2c.

Figure S8. $^1$H NMR spectra of (A) 2c and (B) 1 and (C) P1/2c in chloroform-$d$. The solvent peaks were marked with asterisks.
**Figure S9.** $^{13}$C NMR spectra of (A) 2c and (B) 1 and (C) P1/2c in chloroform-$d$. The solvent peaks were marked with asterisks.

**Figure S10.** IR spectra of (A) 2d and (B) P1/2d.
Figure S11. $^1$H NMR spectra of (A) 2d in dichloromethane-$d_2$ and chloroform-$d$, (B) 1 and (C) P1/2d in chloroform-$d$. The solvent peaks were marked with asterisks.

Figure S12. $^{13}$C NMR spectra of (A) 2d in dichloromethane-$d_2$ and chloroform-$d$, (B) 1 and (C) P1/2d in chloroform-$d$. The solvent peaks were marked with asterisks.
**Figure S13.** $^1$H NMR spectra of 6 in chloroform-$d$.

**Figure S14.** $^{13}$C NMR spectra of 6 chloroform-$d$.

**Figure S15.** Wavelength dependence of the refractive index of a thin film of P1/2a on the UV irradiation time.
Figure S16. (A) Absorption spectra and (B) emission spectra of P1/2 and 4 in THF solution. Solution concentration: 10 μM.

Figure S17. (A) Emission spectra of model compound 4 in THF/water mixtures with different water fractions ($f_w$). (Solution concentration: 10 μM; excitation wavelength: 320 nm). (B) Plot of relative emission intensity ($I/I_0$) versus the water fraction of the THF/water mixtures of model compound 4.
**Figure S18.** (A) Emission spectra of P1/2a in THF/water mixtures with different water fractions ($f_w$). (Solution concentration: 10 μM; excitation wavelength: 310 nm). (B) Plot of relative emission intensity ($I/I_0$) versus the water fraction of the THF/water mixtures of P1/2a. Inset: fluorescent photographs of P1/2a in THF solution and THF/water mixture with 90% water fraction taken under 365 nm UV illumination from a hand-held UV lamp.

**Figure S19.** Emission spectra of (A) P1/2b and (B) P1/2c in THF/water mixtures with water fractions ($f_w$) at 0% and 90%. (Solution concentration: 10 μM; excitation wavelength: 310 nm).
Figure S20. (A) Emission spectra of P1/2d in THF/water mixtures with different water fractions ($f_w$). (Solution concentration: 10 μM; excitation wavelength: 330 nm). (B) Plot of relative emission intensity ($I/I_0$) versus the water fraction of the THF/water mixtures of P1/2d. Inset: fluorescent photographs of P1/2d in THF solution and THF/water mixture with 90% water fraction taken under 365 nm UV illumination from a hand-held UV lamp.